Electromagnetic fields around silver nanoparticles and dimers

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We use the discrete dipole approximation to investigate the electromagnetic fields induced by optical excitation of localized surface plasmon resonances of silver nanoparticles, including monomers and dimers, with emphasis on what size, shape, and arrangement leads to the largest local electric field (E-field) enhancement near the particle surfaces. The results are used to determine what conditions are most favorable for producing enhancements large enough to observe single molecule surface enhanced Raman spectroscopy. Most of the calculations refer to triangular prisms, which exhibit distinct dipole and quadrupole resonances that can easily be controlled by varying particle size. In addition, for the dimer calculations we study the influence of dimer separation and orientation, especially for dimers that are separated by a few nanometers. We find that the largest $|E|^2$ values for dimers are about a factor of 10 larger than those for all the monomers examined. For all particles and particle orientations, the plasmon resonances which lead to the largest E-fields are those with the longest wavelength dipolar excitation. The spacing of the particles in the dimer plays a crucial role, and we find that the spacing needed to achieve a given $|E|^2$ is proportional to nanoparticle size for particles below 100 nm in size. Particle shape and curvature are of lesser importance, with a head to tail configuration of two triangles giving enhanced fields comparable to head to head, or rounded head to tail. The largest $|E|^2$ values we have calculated for spacings of 2 nm or more is $\sim 10^5$.

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I. INTRODUCTION

Although it was discovered nearly a century ago, Mie theory (the classical electromagnetic theory of spherical particles)\textsuperscript{1–3} continues to play a crucial role in describing the optical properties of metal nanoparticles, especially silver and gold particles. One of the important uses of Mie theory is in describing the size dependence of localized surface plasmon resonances; indeed one finds that Mie theory easily describes red shifts and broadening of the dipole plasmon resonance as particle size is increased, as well as the appearance of quadrupole and higher resonance contributions. Recently, new synthetic methods including wet-chemistry methods\textsuperscript{4–6} and lithographic techniques\textsuperscript{7} have provided significant challenges to electrodynamics theory through the production of high yields of nanoparticles with well-defined nonspherical shapes. When spherical metal particles are transformed into nanoscale rods\textsuperscript{8,9} disks,\textsuperscript{10,11} or triangular prisms,\textsuperscript{6} the surface plasmon resonances are strongly affected, typically red-shifting and even splitting into distinctive dipole and quadrupole plasmon modes. In addition, nanoparticle aggregates with controllable dimensions, such as DNA-linked gold nanoparticle assemblies\textsuperscript{12–14} and molecularly bridged metal nanoparticle arrays,\textsuperscript{15} are currently of great interest due to their unique optical and electrical properties, with possible applications in surface enhanced Raman spectroscopy (SERS),\textsuperscript{16–18} electronics,\textsuperscript{15} and biosensors.\textsuperscript{19,20}

All of these factors motivate the need for a theory that can describe the electrodynamics of nanoparticles with arbitrary shapes, degree of aggregation, and complex external dielectric environments.

Over the last 15 years, new theories have been introduced for performing classical electrodynamics studies of light scattering from particles of arbitrary shape, including the discrete dipole approximation (DDA),\textsuperscript{21–23} finite difference time domain methods,\textsuperscript{24} T-matrix methods, the multiple multipole method,\textsuperscript{25} and the modified long wavelength approximation (MLWA).\textsuperscript{21,26} Among them, the DDA is a particularly powerful method for isolated nanoparticles or small aggregates that are in a complex surrounding environment. In the DDA, the object of interest is represented as a cubic array of N polarizable elements.\textsuperscript{23,27} The response of this array to an applied electromagnetic field is described by self-consistently determining the induced dipole moment in each element. This information can be used to determine far-field properties like extinction efficiencies and scattering cross sections, and also near-field properties such as the E-field close to the particle that determines the electromagnetic enhancements in SERS.

Although SERS has been the subject of extensive studies, and a literature consisting of hundreds of papers, a complete understanding of the mechanism of the enhancement is still missing. On the basis of many earlier studies,\textsuperscript{28–34} an important contribution to the SERS enhancement comes from the electromagnetic (EM) enhancement mechanism, in which plasmon excitation in the particle creates an enhanced E-field near the particle, which in turn leads to enhanced Raman excitation and emission. Two types of enhancements are of interest: The average of $|E|^2$ over the particle surface,
which is relevant to conventional SERS measurements, and the peak value of $|E|^2$, which is important in single molecule SERS. In conventional SERS, the Raman enhancement factor is around $10^6$, while in single molecule SERS, the enhancement factor is around $10^{12}$, and this typically gives average $|E|^2$ values of a few hundred, which suggests that most but not all of the enhancement is electromagnetic. However, the situation for single molecule SERS is much less clear, as the properties which determine the peak $|E|^2$ are incompletely known. Peak $|E|^2$ values are relatively modest for isolated spheres (~100), however, they are significantly higher ($>10^5$) for spheroids and nanoparticles, due in part to red-shifted plasmon excitation which gives the metal a more free-electronlike response and to sharp points that produce lightening-rod effects. In many of the theoretical studies, mostly based on quasistatic approximations. Very recently, Lu and coworkers have obtained similarly large enhancements in finite element electromagnetic studies of atomic force microscopy (AFM) tips interacting with spherical silver nanoparticles. These large enhancement estimates have been used in the interpretation of single molecule SERS. For example, Brus and coworkers found that the active nanoparticles for single molecule SERS are compact aggregates consisting of a minimum of two individual particles. Also, Xu and Käll et al. demonstrated that single molecule SERS associated with hemoglobin between two colloidal particles may be subject to $|E|^2$ enhancements as large as $10^5$. However it has never been clarified how the field between two nanoparticles depends on the shape, size, and orientation of the nanoparticles, and in particular what is the highest possible SERS enhancement based on electromagnetic effects. In addition, for monomers or dimers that support multiple plasmon resonances, it is not clear which of the resonances (dipole, quadrupole, etc.) give the largest SERS intensities. This is one reason why there has been confusion as to whether single molecule SERS can occur for molecules on isolated particles or not.

In this paper, we report DDA calculations for Ag nanoparticles and dimers of Ag nanoparticles in which size, shape, orientation and spacing of the nanoparticles are varied over a significant range. Although there have been earlier studies of fields associated with metal particles in two dimensions, here we consider three-dimensional compact particles that are relevant to recent experiments. We especially consider spherical and triangular shapes, as the Ag dimer resonances for these shapes exhibit distinct dipole and quadrupole plasmon resonance features which aid in interpreting the spectra. Our analysis will emphasize peak E-field values, although for completeness we show the complete near-field for many particle shapes and arrangements. Although individual particles will be examined, we find that dimers give maximum E-fields that are a factor of 10 larger than any compact monomer structure, so most of our analysis will be on dimers. E-field enhancement factors as high as $10^5$ are found, and with surprising insensitivity to local radius of curvature, but with strong dependence on particle spacing. We show that the dimer of Ag triangular prisms has great potential in single molecule SERS studies because of the much stronger induced E-fields and unique plasmon resonances at visible and near infrared (IR) wavelengths.

Our calculations are based on local dielectric constants from measurements, which means that we are not including for nonlocal or size dependent dielectric response. The nonlocal description has occasionally been considered, usually for spheres or coupled spheres, with dielectric response modeled using the hydrodynamic or Lindhard–Mermin models. Significant effects are found for small particles (diameter less than 5 nm) typically leading to broader plasmon resonances and smaller SERS enhancements. Size dependent dielectric constants arise because of scattering of the conduction electrons off the particle surfaces, which is an effect which could be important whenever the particle is smaller than the electron mean free path. Both classical and quantum theories of this effect have been developed, as recently summarized by Coronado and Schatz, and for silver particles this again leads to a reduction in SERS enhancements, particularly for particle diameters smaller than 5 nm. Since the particle sizes that we consider in this paper are all much larger than 5 nm, we expect that the nonlocal and size dependent dielectric response will not have a major effect. However, a possibly important exception to this can arise when we consider two large particles that nearly touch. In this case, the strong inhomogeneous fields at the junction could lead to high wavevector excitation in the dielectric response, which will enhance nonlocal contributions. In addition, the use of continuum electrodynamics becomes questionable when the particles are so close together that electron–electron interactions, and electron transfer between particles can occur. Because of this limitation, we will restrict our studies of dimer structures to particles that are with one exception separated by at least 2 nm. In this way we are restricting our modeling to structures that we feel can be described realistically by classical electromagnetic theory.

II. CALCULATIONS

The DDA method has been described in detail elsewhere. All calculations here refer to water as the external dielectric medium. The silver dielectric constant in all calculations has been taken from Palik but smoothed as described by Jensen et al. All the DDA calculations use a cubic grid with a grid spacing of 1 nm unless otherwise noted. This grid spacing leads to high-quality simulations of extinction spectra which are converged with respect to grid spacing. However, convergence for the E-field is more difficult to obtain, as demonstrated in Fig. 1 where we plot $|E|^2$ versus distance from the center of a 20 nm diameter sphere, for a direction through along the polarization vector. Included in the figure are results for grid spacings of 1, 0.5, and 0.25 nm. Note that in the DDA results, the field is not cal-

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calculated directly on the particle surface; instead the closest point is one grid point removed from the surface. The figure shows a factor of 2 increase in the peak field between 1 and 0.5 nm, and a smaller increase in going to 0.25 nm. In addition, we find from Mie theory calculations that $|E|^2$ at the surface should be about 240, which is to be compared with a value of 170 for the first grid point of the 0.25 nm grid spacing, and an extrapolated value of 210 at the sphere surface. Thus, we conclude that convergence of the E-field is approximately achieved for a spacing of 0.25 nm. Unfortunately it would not be possible to do many calculations of interest with this spacing, and an extrapolated value of 210 at the sphere surface should be about 240, which is to be compared with a factor of 2 increase in the peak field between 1 and 0.5 nm.

FIG. 1. The E-field enhancement factor vs the distance away from the center of a 20 nm Ag sphere. The data were taken along the polarization axis. The grid spacings are 1, 0.5, and 0.25 nm.

In the triangle dimer calculations, we have considered two different configurations: Head to head (i.e., tip to tip) and head to tail (i.e., tip to side), in order to determine how the plasmon resonance and E-fields vary with particle orientation. In all dimer studies, we have done calculations with the polarization vector taken in three possible directions, typically the parallel and two perpendicular directions to the interparticle axis. The direction of the $k$-vector is generally of lesser importance, but for calculations where the polarization is parallel to the interparticle axis, the $k$-vector is taken to be perpendicular to the plane of the prism, while for perpendicular polarization, we take the $k$-vector parallel to the interparticle axis.

III. RESULTS AND DISCUSSION

A. Monomers

The electrodynamics of nonspherical metal nanoparticles has long been of interest, especially to estimates of the SERS enhancement factor. However, the absence of analytical theory results for particles other than spheroids has proven to be a serious hindrance, and in fact there are very few accurate studies of particles other than spheres or spheroids. In this section we have studied three particle shapes: Rod, oblate spheroid, and triangular prism. Figure 2 presents the extinction spectra of these three particles, where in all cases the dimensions have been chosen so that the longest wavelength resonance is near 700 nm. The silver rod and spheroid show two important plasmon resonances, one associated with long-axis excitation near 700 nm, and another one with short axis excitation at 360 nm. The extinction spectrum of the Ag triangular prism (with side length=60 nm, snip=0 nm, and thickness=12 nm) shows a strong in-plane dipole of the tips that occurs in the experiments. Thus a 2 nm snip refers to a particle in which 2 nm along the 60 nm edges has been removed from each tip. Two other shapes we have studied are: Oblate spheroids, with an aspect ratio of 3.4:1, and an effective radius (radius that makes the actual volume match $4/3 \pi r^3$) of 15 nm, and a cylindrical rod with an aspect ratio of 2.8:1 and the same effective radius.

FIG. 2. The calculated extinction spectra of a spheroid, a rod, and a triangular prism (with the same effective radius (15 nm). The aspect ratios of spheroid and rod are 3.4:1 and 2.8:1, respectively. The prism has a 60 nm edge dimension with thickness of 12 nm.
plasmon resonance at 700 nm, an in-plane quadrupole resonance at 434 nm, and an out-of-plane quadrupole resonance at 340 nm. (See Ref. 6 for details of the assignment of these features.) Figure 3 presents E-fields for the nonspherical particles in Fig. 2, all for the longest wavelength plasmon resonance near 700 nm. (The shorter wavelength resonances have smaller E-fields so we do not present the results.) The E-field contours show that the maximum enhancement for the dipole resonances occurs at the particle tips. The largest fields ($|E|^2$) for the dipole resonance are 3500 (times the applied field) for the triangular prism, 4500 for the rod, and 4700 for the spheroid at the peak resonance wavelength near 700 nm. For the spheroid and rod, the long wavelength resonance red shifts with increasing aspect ratio, and at the resonance wavelengths, the E-field enhancements increase with increasing aspect ratio while keeping the same effective radius. For the triangular prism, the extinction spectrum is sensitive to its edge length, thickness and snipping. The long wavelength dipole resonance shifts to red when the edge length is increased or the thickness decreased, while snipping moves the plasmon resonance to blue. Although the E-fields around nonsymmetrical particles depend on their sizes and shapes, the largest fields ($|E|^2$) for the long wavelength resonances are several thousand times the applied field for all the particle shapes considered.

For spherical Ag particles with radii less than 20 nm, earlier studies using DDA showed that the maximum E-field enhancement is less than about 200 near the plasmon resonance. The plasmon wavelength associated with this resonance is at about 410 nm. Because the E-field enhancement is wavelength dependent, and the dielectric constant is closer to being free-electronlike at longer wavelengths, it is interesting to examine the sphere E-field enhancement for spheres that are sufficiently large that they have a plasmon resonance near 700 nm where the other particles that we considered above have their resonances rather than at 410 nm. For a sphere with radius of 90 nm, the plasmon resonance occurs at 700 nm, and for this case the E-field enhancement is $\sim 25$. This value is much smaller than for the other particles, but this is to be expected as the particle is much larger and, therefore, would have more radiative damping.
B. Dimer of spheres

One of the most interesting questions raised by recent single-molecule SERS experiments concerns the possibility that single-molecule SERS arises from a “hot” site between two particles, or perhaps at the junction between two or more particles. This possibility was suggested by early theoretical simulations. To study this possibility, we have performed DDA calculations for structures which consist of two particles that nearly touch (a minimal separation of 2 nm was considered, as the use of a local dielectric function description becomes questionable for shorter distances). Touching particles were also considered, but slightly smaller fields were found, so we omit this case from our analysis.

Figure 4 presents the extinction spectrum of a dimer of 36 nm silver spheres that are separated by 2 nm. Included are three spectra: One for polarization parallel to the interparticle axis that shows a strong peak at 520 nm and a shoulder peak at 430 nm, one for perpendicular polarization that shows a peak at 410 nm, and one that corresponds to an average over the three possible polarizations. To assign the resonances, we examined the induced polarization in each DDA element at the three possible polarizations. To assign the resonances, Fig. 7 plots the induced polarizations, but the polarizations at the interface become the largest induced polarization occurring where the tips come together. In contrast, at 550 nm we see the same induced polarizations, but the polarizations at the interface between the prisms are directed oppositely on the two particles.

C. Dimer of triangular prisms

It has already been noted above that isolated nonspherical particles show typically larger $|E|^2$ than for isolated spheres because of their ability to support plasmon resonance at long wavelengths while keeping the effective radii small. It is therefore of interest to see if dimers of nonspherical particles also yield higher $|E|^2$. One issue of significance to this study is where the longest wavelength plasmon resonance occurs. Here we have chosen only to consider dimers that have dipole plasmon wavelengths shorter than 1000 nm, which means that the particle separations are typically a few nanometers or more.

Figure 6 shows the extinction spectra of a pair of triangular prisms that are positioned on a common plane, with a common perpendicular bisector, and with corresponding tips directed toward each other (“head-to-head”) and separated by 2 nm. The extinction spectra and the E-field enhancement contours obtained for polarization along the x and z axes, i.e., perpendicular to the plane of the triangles, and perpendicular to the interparticle axis, are very similar to what is found for uncoupled triangles. However, when the polarization is along the inter-particle axis (y polarized) there is a significant red shifting of the dipole plasmon resonance (from 653 to 932 nm), and an additional weak peak at 550 nm appears, while the in-plane quadrupole peak at 434 nm remains. To assign the resonances, Fig. 7 plots the induced polarizations for the 550 and 932 nm resonances. This behavior is analogous to the sphere dimer results described earlier. For the 932 nm resonance, the induced polarization plot shows that the vectors inside the prisms are aligned along the y axis with the largest induced polarization occurring where the tips come together. In contrast, at 550 nm we see the same induced polarizations, but the polarizations at the interface between the prisms are directed oppositely on the two particles. This indicates that the 932 nm peak is the dipole plasmon resonance, while the 550 nm peak is the quadrupole plasmon resonance.

Figure 8 shows E-field contours for the head to head configuration of the prisms at wavelengths that correspond to...
the dipole and quadrupole plasmon resonances in Fig. 7. For both dipole and quadrupole resonances, we see large enhancements at the tips and the interface, but the three-dimensional (3D) plots show that the maximum enhancement occurs at the interface between the two prisms. The largest fields ($|E|^2$) for dipole and quadrupole resonances are 53,000 and 5700 times the applied field, respectively. For the in-plane quadrupole resonance at 434 nm, the maximum enhancement is at the sides of the two prisms and the field is only 16 times the applied field, very similar to the result for the individual prism.

Figure 9 represents the extinction spectra for a pair of...
triangular prisms with a “head-to-tail” orientation and separated also by 2 nm. Again, the polarizations along the x axis and z axis are very consistent with results for the individual prisms. However, with the polarization along the inter-particle axis (y axis), we see four peaks located at 852, 653, 550, and 434 nm. Examination of the induced polarizations indicates that the 852 and 653 nm peaks are dipolar, while the 550 and 434 nm peaks are quadrupolar.

Figure 10 shows E-field enhancement contours at 653 and 852 nm with the induced polarization along the inter-particle axis. For both dipole and quadrupole resonances, we see that the maximum enhancement occurs at the interface between two prisms. The largest fields (∣E∣²) for dipole resonances at 852 and 650 nm are 57 000 and 3 700 times the applied field, respectively. The fields (∣E∣²) for quadrupole resonances at 550 and 434 nm are 570 and 16 times the applied field, respectively. From the induced polarization and, therefore, the E-field enhancement for the “head-to-head” dimer in Figs. 6–8, we see that the head to head and head to tail arrangements of the triangular prisms give almost identical peak enhancements. However, other properties of the two dimers are quite different. For example, the head-to-head dimer shows much stronger E-field enhancement for the quadrupole resonances at 550 nm.

Figure 11 shows the orientation averaged extinction spectra of head-to-tail dimers with different spacings. The bottom panel refers to 60×12 nm triangles with a 2 nm snip, while the top results are for the analogous dimer of half the size (with side length=30 nm, thickness=6 nm, and snip=1 nm) and half the grid spacing (0.5 nm instead of 1 nm). The results in Fig. 11 show four peaks. Among them, the strongest feature is the dipole peak at 653 nm (or 628 nm for
half-sized prisms). In addition, there is a weaker quadrupole peak at 434 nm and a sharp out-of-plane quadrupole peak at 340 nm that does not change with spacing of the triangles. However, the dipole peak along the interparticle axis is very sensitive to separation distance especially when the two prisms are closely spaced. Thus there is a more than a 100 nm red-shift for the 60 nm particle as spacing decreases from 4 to 2 nm (from 2 to 1 nm for half-size prisms).

The E-field enhancement for the prism dimer in Fig. 11 is also very sensitive to spacing. Figure 12 shows the maximum enhancement for the head to tail configuration as a function of spacing. The figure shows an enhancement that increases by nearly an order of magnitude for a 2 nm change in spacing. The results for the 30 and 60 nm prisms are very similar in appearance, but with the 30 nm result shifted to smaller distances by an amount which scales with the relative sizes of the nanoparticles. This indicates that larger E-field enhancements can be obtained for dimers composed of larger particles. We have furthered tested this conclusion by examining 120×24 nm prisms separated by 4 nm, and we find results that are somewhat smaller than the 60×12 nm particles separated by 2 nm. This indicates that the simple scaling of enhancements with particle size, which is an expected result from the quasistatic approximation, breaks down when the particles are large enough that radiative

FIG. 10. (Color) E-field enhancement contours external to a “tip-to-side” prism dimer described in Fig. 9, for a plane that is along the inter-particle axis and that passes midway through the two particles. In the 3D plots, the axis perpendicular to the selected plane represents the amount of E-field enhancement around the dimer. Left: 852 nm. Right: 653 nm.

FIG. 11. The orientation-averaged extinction efficiency for “tip-to-side” prism dimers with three choices of spacings as noted in the legend. Upper: the prism has a 30 nm edge dimension with thickness of 6 nm and snip of 1 nm, which is referring to a half-size prism. Bottom: The prism has a 60 nm edge dimension with snip of 2 nm and with thickness of 12 nm. 36 480 dipoles are used in both calculations.
damping effects are significant. A more detailed analysis of the dimer junction region (not presented) indicates that the maximum enhancement is located in the middle of the gap between the 60 nm prisms for very close spacing (2 nm), but close to one or the other particles for larger separations (6 nm).

For individual triangular prisms, the in-plane dipole resonance is very sensitive to snipping.\footnote{6,23} Figure 13 shows the orientation averaged extinction spectra for dimers of prisms with different snips. It is interesting that only the in-plane \( z \) axis dipole resonance is sensitive to snipping, with the 5 nm snipped prism giving a peak that is blue-shifted by 50 nm in comparison to the perfect prism. This is not surprising because the dipole peak is mostly associated with \( z \) polarized excitation. The \( y \) axis dipole resonances around 850 nm are weakly sensitive to snipping, but intensities increase if snipped. The maximum E-field enhancement for the \( y \) axis dipole resonances is also not sensitive to snipping, which means that it is not necessary to make a perfect triangular prism to generate a large E-field near a dimer. For SERS studies, the dimer of the snipped prisms could be a better choice than unsnipped prisms because the contact area at the interface is larger for that case, while the enhancement is the same. Note that the lack of dependence of the E-field enhancement to snipping occurs for 850 nm excitation. We have also examined electrostatic fields for the same dimers, and we find that this field is larger for the unsnipped particles than for the snipped particles. Thus it seems that the “lightening rod” effect, which is a concept that comes from electrostatics is less relevant for the plasmon resonant response of dimers. A similar result was noted by Kottmann et al.\cite{48} in their studies of isolated triangular wire structures, but here we find that this effect is even more important for dimers than it was for isolated wires.

We have also studied tail to tail configurations of the dimers, and we find that this leads to a somewhat smaller peak enhancement \( (|E|^2 = 14,000) \) than the head to head and head to tail configurations, however, the contact area associated with the peak intensity is much larger than for the other cases.

**IV. CONCLUSION**

In this paper we have used classical electrodynamics to study the optical properties of isolated silver nanoparticles and pairs of these nanoparticles that are separated by a few nanometers. These particles exhibit distinct dipole, quadrupole and higher multipole plasmon resonances, and excitation of these resonances creates an E-field external to the particles that is important in determining normal and single molecule SERS intensities. Because of this, we have attempted to systematically determine which particles and particle dimers lead to the highest E-fields. For individual particles we find that the largest \( |E|^2 \) values are very similar for triangular prisms, oblate spheroids or cylindrical rods, with \( |E|^2 \) always being less than \( 10^5 \). For a dimer of nanoparticles, we find \( |E|^2 \) values of closer to \( 10^5 \) for structures where the particle separation is 2 nm. The enhancement is a strong function of separation distance, and it scales with particle size such that larger particles give the same enhancements for larger separations. Unfortunately the largest enhancements occur for separations that are too small for classical electrodynamics to be valid, and for which the DDA approach is hard to converge. Other structural properties of the dimer, such as local curvature, are found to play a less important role in determining E-field enhancements, although larger enhancements are generally found for dimers that have longer wavelength dipole plasmon resonances. We find that this lack of sensitivity to particle structure is more noticeable for the field at the plasmon resonance wavelength than it is for the electrostatic field. This suggests that quasi-static calculations may be less accurate for determining peak E-field enhancements than for more averaged properties such as the extinction spectrum.

The lack of sensitivity of peak E-field on subtle details of the dimer structure combined with the large SERS enhancement factor we find \( (|E|^2 = 10^{10\text{ for 2 nm separation}}) \) indicate that many dimer structures should be capable of producing single molecule SERS. In addition, the present results provide support for earlier conclusions\cite{17} that single molecule SERS is associated with compact aggregates consisting of a
minimum of two individual particles. However, the present studies suggest that not all of the single molecule SERS enhancement factor of $10^{12}$ can be ascribed to purely electromagnetic effects.

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